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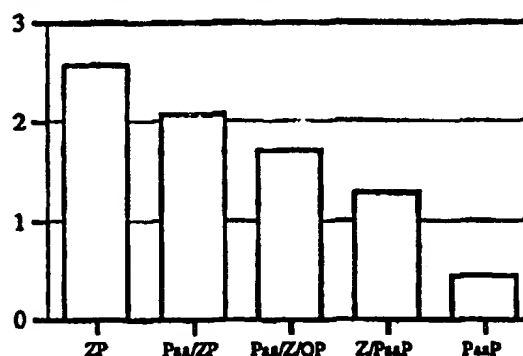
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(54) Title: BLEACHING OF CELLULOSIC PULP WITH OZONE AND PERACID

(57) Abstract

The invention concerns a method for the production of pulp. According to this method, pulp is treated with ozone in at least one bleaching stage. In accordance with the invention, ozone-treated pulp is brought into contact with a peroxy alkanoic acid under acid conditions in order to reduce the pulp's alkali lability, and the resulting pulp is subjected to an alkaline extraction stage or peroxide bleaching stage. The bleaching sequences are thus of the type Z/Paa/E or Z/Paa/P, for example. The pulp produced according to the invention has a kappa number of less than 2, a viscosity of more than 600 ml/g, a tear index (T70) of over 13 mN.m²/g and a zero-span tensile index (T70) as measured from a wet sheet of over 100 N.m/g.

Total carbohydrates dissolved in effluent, kg/tp
Mill P1 pulp, Z/x+ P stages



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Bleaching of cellulosic pulp with ozone and peracid

The present invention relates to a method for the production of bleached pulp with good strength characteristics according to the preamble of claim 1.

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According to such a method, the pulp is treated in at least one bleaching stage in which it comes into contact with ozone.

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The invention also relates to the bleaching sequences according to the preamble of claim 28 as well as to the pulp according to the preamble of claim 32.

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Compared with ECF pulp, ozone-bleached softwood sulphate pulp is known to have a lower viscosity and about 10 % inferior tear strength. Viscosity has been found to correlate closely with tear strength for a given pulp. If the pulp viscosity could be improved, this would be reflected as an improvement in pulp strength.

20

The fall in viscosity is thought to be due not only to depolymerization reactions but also to the alkali-labile carbonyl groups formed during ozonation (1). As a result of this alkali lability, glycosidic bonds in the cellulose chain are broken in the subsequent alkali stage (2).

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It has been suggested that the viscosity of ozonated (Z) pulp can be improved by treatment with borohydride (R), for example using the sequence OZ-R-P, where O = oxygen and P = hydrogen peroxide (3). Treatment with borohydride is based on that the alkali-labile carbonyl groups formed in the pulp during ozonation are reduced by borohydride to alkali-stable alcohol groups (4). The alcohol groups formed in the reduction reaction are not stable, however, and are gradually oxidized back to carbonyl groups, for example on exposure to air. Other drawbacks include the high cost of borohydride and possible problems in treating the effluents.

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Other methods put forward include reducing the carbonyl groups to alcohols with sodium

dithionite (5) and oxidizing them to carboxyl groups with chlorite (6) or hydroxylamine hydrochloride (7).

5 Generally speaking, there are very few bleaching chemicals that can be employed together in the same bleaching stage. One of the chemicals will normally be more reactive than the other, and its bleaching reactions will therefore dominate. To take an example: used together, hydrogen peroxide and chlorine dioxide will react with each other, which means they are less effective together than separately.

10 Treatment with peroxomonosulphuric acid (Caa) has been proposed either prior to, or immediately after, ozone bleaching, the sequence being Caa/Z-E or Z/Caa-E. Research shows that both sequences lead to roughly the same bleaching results (8, 9).

15 Ozone and peracetic acid (Paa) have been used as consecutive stages in an OZPaa sequence and the results compared with those from OZEZ and OZP sequences (10). The pulps used included pine pulp with a kappa number of 20 after the oxygen stage. The highest brightness achieved was 78 - 81 %, even though the ozone charge was around 20 kg/ADt and the peracetic acid charge 20 kg/ADt. In the study cited, prior to ozonation the sulphate pulps were steeped in acetic acid to which dimethylsulphoxide had been
20 added. The problems associated with these solvents relate to fire hazards and the difficulty of their recovery from the bleaching filtrates.

In a more established procedure, peracetic acid, ozone and oxygen have been employed under acidic conditions in a single stage (FI Patent Application No. 940412, reference 11).
25 In this well-known procedure, the pulp is first treated with peracetic acid, which reacts with lignin and opens up the pulp's fibre structure. Peracetic acid treatment allows the use of a smaller ozone charge, which in turn reduces fibre damage. It is believed that treating the pulp with only small amounts of ozone will produce a stronger pulp than that obtained with the three-stage treatment O-Z-Paa. In accordance with FI Patent
30 Application No. 940412, ozonation is followed by an alkaline extraction stage using either chlorine dioxide or peroxide.

In other known bleaching experiments, pulp has been treated with ozone, peroxide and peroxy acids such as peracetic acid. In their report, Kinell et al. compared pulps bleached with peroxide combined with ozonation, ozone and peracetic acid treatment, and peroxy acid treatment alone, with pulps bleached using chlorine dioxide (12). The authors
5 concluded that ozone bleaching is not suitable for the production of good-strength pulps.

The use of peroxy acids and hydrogen peroxide in conjunction with ozone bleaching has also been studied by Nin and Ooi (13) using the sequences ZE(O)PaaQP and ZE(O)QPPaa. Based on the results, the authors proposed that hydrogen peroxide be
10 employed before peroxy acid in the early stages of the bleaching sequence, where there are still large amounts of residual lignin.

WO Published Application No. 92/21814 describes a bleaching sequence in which an ozone stage and a washing stage are followed by a Paa stage employing 2 % peracetic
15 acid and 3 % NaOH. The slurry is then maintained at a temperature of 70 °C for 240 min. When the instructions in the publication are followed, the pH is 10.6 at the start of the Paa stage and 10.2 at the end. The alkali lability resulting from the treatment of ozonated pulp under these alkali conditions causes depolymerization and a decrease in pulp strength.

20 For the sake of completeness, it can be added that the use of a solvent such as an alcohol, aldehyde or carboxylic acid has been proposed as a way of improving the selectivity of ozonation. The main purpose of the solvent is to capture the harmful radicals formed during ozonation. Other proposed solvents include urea-methanol, methanol, DMF and DMSO. However, these are expensive and also present problems in relation to effluent
25 treatment and cycle closure.

The purpose of the present invention is to overcome the drawbacks of the prior art and to provide an entirely novel type of a process for the ozone bleaching of pulp.

30 It is also the purpose of the invention to provide new bleaching sequences and to produce a pulp that is new in terms of its characteristics.

The present invention is based on the surprising fact that the treatment of an ozonated pulp with an oxidizing agent under acidic conditions can reduce or completely eliminate pulp alkali lability. The acid stage can be carried out either after washing or without any prior washing stage. In the next stage, residual lignin is extracted from the pulp fibres under alkaline conditions without breaking the cellulose chains. The alkali extraction can be performed with or without prior washing using peroxide and/or peroxide reinforced with oxygen.

According to a preferred embodiment, fully bleached pulp (ISO brightness > 87.5 %) with a kappa number of less than 2, a viscosity greater than 600 ml/g, a tear index (T70) of more than 13 mN·m²/g, and a zero-span tensile index (T70) of over 100 N·m/g measured for a wet sheet can be produced by means of the treatment.

The invention can be applied in practice using bleaching sequences containing Z, Paa and P and/or E stages in this order, one essential requirement being that the Z stage is not followed by an alkali treatment stage before the ozonated pulp has been treated with an oxidizing agent, in particular a peroxy alkanoic acid.

More specifically, the method according to the invention is characterized by what is stated in the characterizing part of claim 1.

The bleaching sequences according to the invention are characterized by what is stated in the characterizing part of claim 28; the pulp according to the invention is characterized by what is stated in the characterizing part of claim 32.

As stated above, the invention can be used to reduce the alkali lability of ozonated pulp by bringing the pulp into contact with an oxidizing bleaching agent under conditions that are acid (including neutral or at most slightly acid conditions). Although we do not fully understand the mechanism underlying the bleaching process, it seems clear that this kind of treatment reduces the number of carbonyl groups in the pulp, which in turn means less hydrolysis of glycosidic bonds in the alkali stage following the acid stages. This finding

has to be regarded as surprising, since it is previously known that the carbonyl group content of pulp increases as a result of a treatment with performic and peracetic acids. As the experimental results presented below will show, the carbonyl group contents of pulps to be bleached in accordance with the invention are doubled during ozonation, whereafter these contents clearly fall by 10 - 15 % (in some cases 20 %) as a result of treatment with peracetic acid subsequent to ozonation. By washing the pulp between the ozone and peracetic acid stages the carbonyl content can be further reduced (by just under 30 %). Unlike the solution according to the WO Published Application (see above), the method according to the invention treats Z pulp with peracetic acid under acidic conditions prior to the alkaline stage, thereby oxidizing some of the carbonyl groups to carboxyl groups. As a result, the pulp undergoes far less depolymerization during the subsequent alkaline stage. The pH at the start of this treatment is acid, neutral or slightly acid (e.g., approx. 4.5 - 8), while the final pH is acid (usually approx. 4.5 - 5).

In addition to reducing the carbonyl group content, the method according to the invention reduces the amount of carbohydrates dissolving under alkaline conditions. Carbohydrate dissolution is at least 30 % lower than in cases where the pulp is treated under alkaline conditions after ozonation. Preventing the dissolution of carbohydrates helps to improve tear strength, the strengths of individual fibres (zero-span strength) and yield, and also to reduce the solute content of the filtrate.

The invention also offers other significant benefits. For example, the method does not employ organic solvents or other compounds that would capture radicals because the carbonyl groups formed by unwanted reactions are removed by the after-treatment according to the invention.

The method according to the invention produces high-brightness pulps by reducing the residual lignin content before ozone treatment and carrying out an alkali treatment at the end of the bleaching stage, yielding pulp with 85 - 92 % brightness (sequence OOPaaO or OOPaaE, for example). Performing the alkaline treatment immediately after the Paa treatment also allows unreacted peroxide to be utilized at the high pH, thus leading to

higher brightness.

The method disclosed in the present invention allows the use of higher ozone charges than in the process described in reference 11, provided that the pulp is subsequently
5 subjected to oxidation, for example with peracetic acid, under acidic conditions. Since the use of ozone as a bleaching agent is fairly economical in the long term, the present invention also offers economic benefits.

Another benefit of particular significance is the fact that the bleaching process described
10 lends itself to process cycle closure. The filtrate from the alkaline extraction stage immediately after peroxy acid treatment can be recycled, in some cases without treatment, for use in oxygen delignification, or else it can be processed without problems in a recovery boiler.

15 In the following, the present invention will be examined more closely with the help of a detailed description and working examples. The diagrams appended provide graphic representations illustrating the results from the working examples, as follows:

Figure 1 shows pulp delignification for different bleaching sequences,

Figure 2 shows the development of brightness,

20 Figure 3 shows hydrogen peroxide consumption in the final P stage of the bleaching sequence,

Figure 4 shows the tear indexes of the bleached pulps,

Figure 5 shows the zero-span indexes (wet) of the bleached pulps,

Figure 6 shows the carbohydrate contents of the bleaching filtrates separately,

25 Figure 7 shows the total carbohydrate contents of the bleaching filtrates per tonne of bleached pulp,

Figure 8 shows the tear indexes of Z/Paa/EP pulp for different ozone and Paa charges, and

Figure 9 shows the zero-span tensile index (wet) of Z/Paa/EP pulp.

30 According to the invention, the bleaching sequence for pulp includes the following stages:

-Z/Paa/P,
-Z -Paa/P,
-Z/Paa -P,
-Z/Paa/E,
-Z/Paa -E,
-Z/Paa/EP,
-Z/Paa/E_R,

5

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where Z = ozone stage, Paa = peroxy acid stage, P = peroxide stage, E = alkaline extraction stage, R = an alkaline stage involving borohydride, O = oxygen delignification stage, and the hyphen (-) indicates a washing stage. The Z stage should preferably be preceded by a peroxide (P) or pressurized peroxide (PO) stage.

15

According to the invention, the pulp pH is not allowed to rise too well on the alkaline side between ozonation and treatment with oxidizing bleaching agent in order to avoid the dissolution of carbohydrates that would result at alkaline pH from the formation of alkali-labile groups through the reactions of ozone. The pH should preferably be kept between 2 and 8, the preferred pH being around 4.5 - 8 at the start and about 2.5 - 6 at the end.

20

Ozone treatment and treatment with an oxidizing bleaching agent are performed either in the same bleaching stage or in different stages. Ozone treatment and treatment with an oxidizing bleaching agent can be carried out more or less simultaneously, or else the pulp can first be treated with ozone and then with an oxidizing bleaching agent. The simultaneous use of ozone and peroxy acid has not been found to cause any problems.

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According to one preferred embodiment of the invention, the total oxidation equivalent to be used in bleaching is divided more or less equally between ozonation and peroxy acid treatment. Accordingly, ozone normally accounts for 30 - 90 % (preferably about 40 - 70 %) of the oxidation equivalent used in bleaching, while the peroxy acid accounts for 70 - 10 % (preferably about 60 - 30 %) of the oxidation equivalent used in bleaching.

The oxidizing bleaching agent used according to the present invention is a peroxy acid such as a lower peroxy alkanoic acid, more particularly performic acid, peracetic acid or perpropionic acid, or peroxomonosulphuric acid (Caro's acid) or mixtures thereof. Peracetic acid, which is a particularly suitable peroxy alkanoic acid, is prepared by reacting acetic acid with hydrogen peroxide in the molar ratio 1:1 - 1:2 with a small amount of sulphuric acid as catalyst. Peracetic acid is used either as an equilibrium product or in distilled form. Typical conditions for a peracetic acid stage are: peracetic acid charge 2 - 40 kg/BDt, pH 3 - 8, temperature 50 - 90°C and reaction time 30 min - 6 hours. If necessary, the peracetic acid stage can include additives, e.g. magnesium sulphate and/or a chelating agent such as EDTA or DTPA, at the rate of 0.5 - 3 kg/BDt. Particularly suitable conditions for a peracetic acid treatment are: pH 4.5 - 7, reaction time 30 - 180 min, and temperature 50 - 80°C.

For the ozone stage, typical conditions include a pulp consistency of 1 - 40 % (i.e. low, medium or high consistency). The ozone gas used for bleaching is a mixture of ozone and oxygen, usually containing 5 - 15 % ozone. The optimum pH for ozonation is between 2 and 5, preferably about 3. The pH is usually adjusted with sulphuric acid, although organic acids can also be used. With very low ozone charges (under 2 %), a higher pH (5 - 10) can be employed. However, in this case some of the ozone decomposes and the charge therefore has to be increased to make good the loss. The temperature in the ozone stage can be 0 - 80°C. In industry, ozonation is performed at a temperature of around 50 - 70°C. A high temperature has the same kind of impact as high pH. The ozone charge is 0.5 - 15 kg/BDt, usually 2 - 6 kg/BDt, the charge depending on the kappa number of the incoming pulp. A high kappa number requires a greater ozone charge than a low kappa number.

According to one preferred embodiment, the pulp is washed with water between the ozone and peroxy acid stages until it appears neutral or only slightly acidic. This washing further reduces the content of dissolved carbohydrates, improves both tear index and brightness, and appears to lower the content of carbonyl groups. Washing can be carried out in the usual way in one or more stages, with the water displaced from the pulp

between washing stages by filtration.

The pulp going forward to the alkali stage has a carbonyl group content of at least 10 %, usually at least 15 %, less than the pulp coming to the ozone stage. This means that
5 certain typical sulphate pulps contain less than 14 milli-equivalents of carbonyl groups per kg of pulp when the pulp is bleached using 625 kg of oxidation equivalents (OXE)/tonne.

In this invention, the alkaline treatment stage following the peroxy acid stage comprises any known treatment stage in which the pH of the pulp is made alkaline, i.e. raised to a
10 pH of at least 8, preferably of around 10 - 12.

Suitable alkaline stages include alkaline extraction (usually abbreviated E), possibly incorporating treatment with another chemical such as borohydride (R) or peroxide (P); an oxygen stage (O), a hydrogen peroxide stage (P, PO), and combinations thereof. The
15 conditions for the alkaline stage correspond to those in known bleaching sequences. The borohydride charge is usually about 0.1 - 10 kg/BDt. The amount of peroxide used is generally 5 - 60 kg/BDt (0.5 - 6 %), which may be divided between the peroxide stage preceding ozonation and the peroxide stage following peroxy acid treatment.

To summarize what has been said above, one preferred embodiment of the invention would be as follows: ozone stage using approx. 1 - 8 kg ozone/BDt (0.1 - 0.8 %), peroxy acid stage using approx. 1 - 30 kg peroxy acid/BDt (0.1 - 3 %), peroxide stage preceding
20 ozonation using approx. 5 - 30 kg hydrogen peroxide/BDt (0.5 - 3 %), and peroxide stage following peroxy acid treatment using approx. 1 - 20 kg hydrogen peroxide/BDt (0.1 - 2
25 %).

The pulp to be subjected to ozone bleaching may be chemical, chemi-mechanical or mechanical pulp. One very common type of pulp in this context would be oxygen-delignified sulphate pulp, more particularly oxygen-delignified softwood pulp. In addition
30 to oxygen delignification, the pulp may be subjected to other treatments with agents such as enzymes, complexing agents and peroxide, depending on the treatment stages following

ozonation. Examples of bleaching stages that may be used prior to ozonation include the following sequences:

- 5 -O/O-X/Q-(PO),
 -O/O-X/Q-P,
 -O-O-Q-P, and
 -O/O-X-Z/Paa/Q-P,

10 where X refers to pulp treatment with an enzyme and Q refers to a stage involving a complexing agent. The abbreviations O, P, PO, Paa and Z have the same meanings as given earlier.

The pulp entering the ozone stage generally has a kappa number of about 2 - 16, preferably about 2 - 10.

15 The treatment specified in the present invention yields a pulp with good strength characteristics and, depending on the bleaching sequence used, an ISO brightness of at least 85 units, usually over 87 units. The pulp has a kappa number of less than 2, in some cases under 1.8, a viscosity greater than 620 ml/g (closer to 700 ml/g, depending on the temperature of the peroxy acid stage), a tear index (T70) of over 14 mN·m²/g and a zero-span tensile index (T70), measured from wet sheets, of over 105 N·m/g. The zero-span tensile index (wet sheet) can be raised to almost 115 N·m/g by washing the pulp between the peroxy acid stage and the alkali stage. The tear index is preferably over 14.5 mN·m²/g.

25 As stated above, the bleaching sequences specified in the invention can be made part of cycle closure. This especially applies to sequences that do not contain a separate complexing agent stage (Q). The filtrate from the alkaline extraction stage is recovered and returned, at least in part, to pulp cooking, oxygen delignification or bleaching.

30 Performing an alkali treatment immediately after the acid stages facilitates both filtrate handling and cycle closure. From the point of view of cycle closure, the following

sequences according to the invention are particularly favourable: OOPaa/Z/Paa/E, OOQPZ/PaaO and OOQPZ/Paa/E. As the use of chelating agents in peroxide bleaching is essential for control of harmful metal ions and retention of viscosity, a sequence ending in an E or O stage, as specified in the invention, reduces the charge of chelating agent used.

One preferred embodiment is an alternative in which the alkali stage is performed after peroxy acid treatment without intermediate washing, whereby the filtrate from the alkaline extraction stage contains at least some peroxy acids, which form hydrogen peroxide. This filtrate can be recycled direct to oxygen delignification and to suitable peroxide stages.

To avoid the use of chelating agent completely, a sequence according to the invention can be used, such as OOXpaa/Z/Paa/O, where X represents an enzyme treatment. The principal enzymes used are hemicellulase or ligninase types such as xylanases and/or mannanases and laccase.

The following non-limiting examples illustrate the invention.

Example 1

These experiments were conducted using mill softwood sulphate pulp. An equilibrium solution of peracetic acid was prepared from 50 % hydrogen peroxide and 100 % acetic acid. The $\text{CH}_3\text{COOH} : \text{H}_2\text{O}_2$ molar ratio was 1.67. The softwood sulphate pulp from the digester had a kappa number of 24.1, a brightness of 32.8 % and a viscosity of 1050 ml/g. The pulp was delignified to the kappa number 10 using the sequence O/O-Q, and bleaching was continued with a PO stage.

The PO pulp had a kappa number of about 6, a brightness of about 75 % and a viscosity of 760 - 790 ml/g. The pulp was then bleached using sequences according to the invention and also with reference sequences, as follows: Z-P, Z/Paa-P, Z-Paa-P, Z/D-P, Z/R-P and D-EOP-D. Calculated in terms of oxidation equivalents, the same amounts of chemicals

were charged to the Z, Z/Paa, Z-Paa and Z/D stages, i.e. 625 kg OXE/BDt. Based on the total OXE charge, the amount of ozone used was 50:50 in relation to the peracetic acid or chlorine dioxide ratio. Based on optimization experiments, the borohydride charge to the Z/R stage was 10 kg/BDt and the ozone charge 5 kg/BDt.

5

The bleaching conditions are shown in Table 1.

Table 1. Conditions used in the O/O, Q, PO, Z, Z/Paa, Z-Paa, Z/D, Z/R, P and D-EOP-D bleaching stages.

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Stage	Consistency %	Temperature °C	Time min	Initial pH	Chemical charge kg/BDt
O/O	10	100	45/60		NaOH 25/10, MgSO ₄ 5, O ₂ pressure 8/6 bar
Q	8	80	60	5	DTPA 3
PO	12.5	90	120		H ₂ O ₂ /NaOH 20/20, DTPA-/MgSO ₄ 2/2.5, O ₂ pressure 6 bar
Z	12.5	50	10	3	O ₃ 5
Paa	12.5	70	120	5	Paa 23.8, DTPA/MgSO ₄ 2/2.5
Z/Paa	12.5/10	50/50	10/180	3/5	O ₃ /Paa 2.5/12.7, DTPA/Mg-SO ₄ 2/2.5
Z-Paa	12.5/10	50/70	10/120	3/5	O ₃ /Paa 2.5/12.8, DTPA/MgSO ₄ 2/2.5
Z/D	12.5/10	50/50	10/60	3/3	O ₃ /ClO ₂ 2.5/4.2
Z/R	12.5	50/50	10/60	3/10	O ₃ /NaBH ₄ 5/10
P	12.5	90	180	10.3	H ₂ O ₂ /NaOH 15/20, DTPA/MgSO ₄ 2/2.5
D	8.0	69	60	-2.6	ClO ₂ 19.2/
EOP	10.0	70	60	- /10.1	NaOH, H ₂ O ₂ 3
D	10.0	75	180	-4	ClO ₂ 20

The characteristics of the pulps are shown in Table 2.

Table 2. Characteristics of the Z, Z/Paa, Z-Paa, Z/D, Z/R and D-EOP-D pulps.

	O/O-Q-PO	Z-P	Z/Paa-P	Z-Paa-P	Z/D-P	Z/R-P	D-EOP-D
Kappa no.	6	1.4	2.5	1.1	1.4	1.7	0.8
Brightness, %	75	88.9	81.7	88.9	91.1	89.5	88.1
Stand. visc., ml/g	780	610	650	680	680	680	730
Borohydride visc., ml/g	770	670	650	680	680	680	730
Δ visc., ml/g*)	10	60	0	0	0	0	0
Yield, %	99.3	89.9	99.1	99.1	99.0	99.4	not def.
P consumption, kg/BDt	10.2	5.9	2.8	4.9	5.8	4.4	

*) Difference between borohydride and standard viscosities.

The results indicate that ozone, peracetic acid, chlorine dioxide (oxidizing agents) and borohydride (reducing agent) function well together. Washing between the Z and Paa stages improved delignification to some extent. The H_2O_2 consumption in the final P stage of the bleachings Z/Paa-P and Z-Paa-P was approx. 5 kg/BDt. In Z-P bleaching the consumption was much higher. The contents of carbonyl and carboxyl groups of the pulps and the differences between standard and borohydride viscosities are shown in Table 3.

Table 3. Carbonyl and carboxyl group contents, and differences between standard and borohydride viscosities for Z, Z/Paa, Z-Paa, Z/D and Z/R pulps.

Sequence		Z	Z/Paa		Z-Paa		Z/D		Z/R	
Pulp	PO	Z	Z	Paa	Z	Paa	Z	D	Z	R
Carbonyl content, mmol/kg	8.9	17.2	15.2	12.0	14.3	10.9	15.2	15.5	17.2	2.4
Stand. visc., ml/g	780	650		680		710		720	650	710
Boroh. visc., ml/g	790	710		700		710		740		
Δ visc. (boroh. - stand.), ml/g	10	60		20		0		20		60

As can be seen from the Table; ozonation causes a doubling of the pulp's carbonyl content. In the sequence Z/Paa, the carbonyl content falls from 15.8 to 12.0 mmol/kg during the Paa treatment subsequent to the Z stage. Washing the pulp between the ozone and Paa stages (Z-Paa) lowered the carbonyl content still further (14.3 to 10.9 mmol/kg) after the Paa treatment. The alkali lability of ozone-bleached pulp falls significantly during Paa treatment, which is also reflected in the fact that the difference between borohydride and standard viscosities is only 0 - 20 ml/g.

Table 4 shows the bleaching results and papermaking characteristics of the pulps at a tensile index of 70 N·m/g (T70).

Table 4. Bleaching results and papermaking characteristics obtained with Z-P, Z/Paa-P, Z-Paa-P, Z/DP, Z/R-P, Paa-P and D-EOP-D sequences.

Sequence	Kappa number	Brightness %	PFI revs. (T70)	Tear index (T70) mN·m ² /g	Zero-span dry (T70) N·m/g	Zero-span wet (T70) N·m/g
PO pulp	6.0	75.0				
Z-P	1.4	88.9	1963	13.1	149	91
Z/Paa-P	1.5	87.8	1577	14.1	144	105
Z-Paa-P	1.1	88.9	1533	14.5	139	114
Z/DP	1.4	91.1	1630	14.8	149	113
Z/RP	1.7	89.5	1916	15.2	150	108
Paa-P	1.7	87.7	1935	14.8	156	114
D-EOP-D	0.8	88.1	1785	14.3	143	124

The results from the above Table are presented graphically in Figs. 1, 2, 4 and 5.

Figure 3 presents hydrogen peroxide consumption in the final stage of the sequences Z-P, Z/x-P, ZxP, x/Z-P and Paa-P.

The Table shows that the strength of the TCF₂ pulp can be improved by 13 - 16 % by including in the ozone stage an oxidative treatment at acid conditions with

peracetic acid (Paa) or chlorine dioxide (D), or reduction with borohydride (R) without intermediate washing. An even better kappa reduction, brightness and tear index than for the Z/Paa-P pulp were obtained with the sequence Z-Paa-P, i.e. with intermediate washing. Zero-span tensile indexes measured from wet sheets were 14 - 23 units (15 - 25 %) greater for the Z-Paa-P than the Z-P pulp.

Example 2

A mill pulp subjected to the treatment O-Q-O-P1 was bleached using the sequences P-Z-P, P-Paa/Z-P, P-Paa/Z/Q-P, P-Z/Paa-P, P-Z/R-P and P-Paa-P. The conditions used in the Z/x-P sequences (x = Q, Paa, Caa and NaBH₄) are shown in Table 5.

Table 5. Bleaching conditions used in the Z, Paa, Z/x, x/Z and P2 stages.

Stage	Chemical charge kg/BDt	DTPA- /MgSO ₄ kg/BDt	Final pH	Temperature °C	Reaction time min	Pulp consistency %
Z	5		3	50		12.5
Z/Q	5/2		3/5	50/50	/60	12.5/12.5
Paa/Z	varied	2/2.5/	3.8/3.5	50/50	60-180/	12.5/12.5
Z/Paa	2.5/11.9	/2/2.5	3/5	50/50	/180	12.5/10
Z/R	5/10		3/10	50/50	/60	12.5/12.5
Paa	23.8	2/2.5	5	180-90	120	12.5
P	H ₂ O ₂ /NaOH 20/15	2/2.5		90	180	12.5

The carbonyl contents and viscosities of the pulps are presented in Table 6.

Table 6. Pulp carbonyl contents and viscosities.

Stage	Z	Paa/Z	Z/R	Z/Paa	Paa
Chemical charge, kg/BDt	5.0	11.9/2.5	5/5	2.5/11.9	24
Carbonyl content, mmol/kg	15.8	12.9	9.8	11.3	9.9
Stand. viscosity, ml/g	660	690	700	720	750
Borohydride viscosity, ml/g	720	730	700	740	750
Δ visk. (boroh. - stand.), ml/g	60	40	0	20	0

The high carbonyl content of the Z pulp is clearly reflected in the difference between borohydride and standard viscosities, which was 60 ml/g. The corresponding difference in the case of the Z/Paa and Z/R pulps was much smaller (0 - 20 ml/g).

The kappa numbers, brightnesses and papermaking characteristics of the pulps are shown in Table 7.

Table 7. Bleaching results and papermaking characteristics (T70 = PFI beating to a tensile index of 70 N·m/g) of the pulps.

Sequence	Kappa number	Brightness %	PFI revs. (T70)	Tear index (T70) mN·m ² /g	Zero-span dry (T70) N·m//g	Zero-span wet (T70) N·m/g
P1 pulp	6.8	75.8	939	13.4	147	121
ZP	1.8	88.3	1642	12.1	144	102
Paa/ZP	1.8	88.0	1840	12.3	138	101
Paa/Z/QP	2.0	87.9	1517	12.3	142	100
Z/PaaP	1.8	88.0	1467	13.2	150	109
Z/RP	2.0	88.9	1417	13.0	150	102
PaaP	1.9	88.0	1659	12.9	138	115

As Table 7 shows, the tear index of Z/PaaP pulp bleached using the sequence according to this invention is 1.2 units higher than that of pulp bleached with the reference sequence ZP.

Example 3

The bleaching experiments according to the invention were performed on softwood sulphate pulp with a kappa number of 16 and a viscosity of 810 ml/g that had been oxygen-delignified (O) at the mill. The pulp was subjected to chelation with EDTA (Q) at pH 5 and then pre-bleached with oxygen in a pressurized peroxide stage (PO). The hydrogen peroxide charge in the peroxide stage was 20 kg/BDt (consumption 13 kg/BDt), the alkali charge 20 kg/BDt, pH 10.5, temperature 80°C, reaction time 180 min and pressure about 6 bar. The additives were DTPA (5.5 kg/BDt) and MgSO₄ (2.5 kg/BDt). The kappa number was reduced to 5.6 by this treatment.

Ozone bleaching (Z) was performed at medium consistency with an ozone charge of 0.5 kg/BDt (consumption 3.6 - 4.0 kg/BDt) at 50°C and pH 3. The peracetic acid stage (Paa) was carried out, without washing, using a distilled peracetic acid product with charges of 5, 15 or 20 kg/BDt (consumption 5, 10 and 12 kg/BDt) at 70°C and pH 5 using a reaction time of 180 min. In the subsequent alkaline extraction stage (E), which was also performed without washing, the NaOH charge was 20 kg/BDt, which raised the pH to 10.5. The reaction time was 60 min and the temperature 70°C.

After the Z/Paa/E stages, the pulps were washed and the pH adjusted to 4.5 with sulphur dioxide.

In one experiment, the E stage was boosted with a small (3 kg/BDt) peroxide charge (Ep stage). In another experiment, borohydride (0.5 kg/BDt) was used in the E stage. In the experiment with the lowest peracetic acid charge (5 kg/BDt), the E stage was replaced by a peroxide stage (P) without intermediate washing, the hydrogen peroxide charge being 10 kg/BDt (consumption 5 kg/BDt).

For comparison, the same ozonated pulp was subjected to an alkaline peroxide

stage (P) without any oxidative treatment under acid conditions. The sequence was thus O/O-Q-PO-Z-P. The effects of these treatments on pulp viscosity are shown in the Table below. A duplicate series of experiments was performed to confirm the results (Table 8).

5

Table 8. Effects of the bleaching sequences according to the invention on the characteristics of bleached sulphate pulp. T70 = tensile index 70 N·m/g.

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	Kappa no.	Brightness %	Stand. visc. ml/g		Kappa no.	Brightness %	Stand. visc. ml/g
<u>Series 1</u>				<u>Series 2</u>			
Z-P (comp.)	1.7	88.9	580	Z-P (comp.)	1.6	88.0	590
Z/Paa/E	1.2	88.7	650	Z/Paa/E	1.2	87.8	630
Z/Paa/Ep	1.2	89.1	650				
Z/Paa/Er	1.3	88.7	670	Z/Paa/Er	1.3	88.1	650
Z/Paa/P	1.6	88.7	620	Z/Paa/P	1.4	88.1	610

15

Tear index (T70) Z/P: 12.4 mN·m²/g

20

Z/Paa/E 13.4 "

Zero-span tensile index (T70) measured from wet sheet:

Z/P: 104 N·m/g

Z/Paa/E 106 "

25

As can be seen from the Table, after the treatment according to the invention the pulp viscosities were 40 - 90 viscosity units higher than those of the reference (Z-P) pulps.

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Example 4

The effects of borohydride (R stage) and peracetic acid (Paa stage) have been compared using the same ozone-treated pulp (ozone charge 5 kg/BDt). The borohydride and peracetic acid charges used were 0, 2.5, 5, 7.5 and 10 kg/BDt. Peroxide (P stage) was used for final bleaching. The pulp viscosities resulting from said reducing (R) and (Paa) stages according to the invention are shown in Table 9.

Table 9. Effects on Z pulp characteristics of a reducing agent (borohydride, R stage) and of an oxidizing agent (peracetic acid, Paa stage) according to the invention. Starting pulp: O/OQ(PO) pulp, kappa no. 7.3, brightness 72.8 % and viscosity 790 ml/g.

NaBH ₄ or Paa charge/BDt	Kappa number	Brightness %	Viscosity ml/g	Kappa number	Brightness %	Viscosity ml/g
	Z/RP	Z/RP	Z/RP	Z/PaaP	Z/PaaP	Z/Paa/P
0.0	1.9	88.1	610	2.1	87.3	630
1.0	2.1	87.4	620	2.1	87.4	670
2.5	1.9	88.8	640	2.1	87.6	670
5.0	1.9	89.1	660		88.2	660
10.0	1.9	89.4	660	1.7	88.2	670

As Table 9 shows, the borohydride (R stage) and peracetic acid (Paa stage) are equally effective in delignifying ozone-treated pulp and removing its alkali lability.

Example 5

The method according to the invention can be used in environment-friendly processes in order to assist water cycle closure in a bleaching plant without the need for chelation and/or treatment of the acid filtrates. The use of ozone and peracetic acid together in the same stage was tested using the sequences O-O-Paa/Z/Paa and O-O-Z/Paa/E. As neither bleaching sequence involves a peroxide stage (P or PO), there is no need for a separate chelation stage or the special treatments that such a stage necessitates. Another advantage of this type of sequence is that it does not increase the sulphur load to the recovery system because pH adjustment is performed with peracetic acid instead of sulphuric acid. The bleaching results obtained are presented in Table 10.

Table 10. Results from environment-friendly bleaching sequences O-O-Paa/Z/Paa and O-O-Z/Paa/E. Starting pulp: O-O pulp, kappa no. 8.2, brightness 51.7 % and viscosity 780 ml/g.

Sequence	Chemicals charges/consumptions kg/BDt	Kappa number	Bright- ness %	Visc. ml/g
Paa/Z/Paa/E	O ₃ 6/5.2, Paa 15/14.8, 20/19.9, NaOH 35	1.5	81.2	500
Z/Paa/E	O ₃ 6/4.6, Paa: 20/19.9, NaOH 22	1.8	79.3	530

As can be seen from Table 10, both sequences result in a low kappa number and thus good brightness stability.

One of the environment-related targets at pulp mills is to reduce the loadings from bleaching. From this point of view, minimum carbohydrate dissolution during the bleaching stages would be an advantage. Figure 6 shows the carbohydrate contents of the bleaching filtrates individually and in total per tonne of bleached pulp.

As Figure 6 shows, use of the sequences according to the invention roughly halves the amount of carbohydrates found in the filtrates. Replacing some of the ozone charge with peracetic acid reduces the amount of oxalic acid formed through ozone reactions, thus easing the problem of oxalate precipitation. No oxalate precipitation occurs in Paa bleaching. The present invention is thus particularly useful in helping to achieve water cycle closure at pulp mills.

Example 6

Table 11 below presents the optimum pH range for a combined ozone and peracetic acid stage (Z/Paa), though without restricting the invention to this. Experiments were performed using a softwood sulphate pulp pre-bleached using the sequence O-O-Q-(PO) to kappa number 5.5 and 74 % brightness. Final bleaching was performed with the sequence Z/Paa/E. The ozone charge was 5 kg/BDt and the temperature 50 °C. The Paa stage was carried out with a peracetic acid charge of 15 kg/BDt at 70 °C for 180 min. Also shown in the Table is the effect on bleachability of a pressurized Paa stage. In this case the ozone charge was only 2.5 kg/BDt, the peracetic acid charge only 10 kg/BDt, the temperature 50 °C and the reaction time 60 min.

Table 11. Effect of pH in Z/Paa stages on the bleachability of softwood sulphate pulp using the sequence O-O-Q(PO)-Z/Paa/E according to the invention.

O ₃ charge/conc. kg/BDt	Paa charge / conc. kg/BDt	pH in stage Z Paa	Kappa no., final	Brightness, final, %	Viscosity, final, ml/g
<u>Unpress. Paa:</u> 5.1/3.6	15/10.2	3 3	1.1	88	660
4.9/3.7	15/11.6	3 5	1.1	87	640
5.1/3.9	15/11.9	5 5	1.3	85	640
<u>Pressurized Paa:</u> 2.5/1.9	10/5.3	3 5	1.8	85	670

As the Table shows, the highest brightness is achieved by performing the Z stage at pH 3. The results also reveal that the economic benefit achieved using the invention can be improved not just by omitting washing stages but also by pressurizing the peracetic acid stage. This reduces the amounts of chemicals needed and/or the reaction temperature in the Paa stage and/or the reaction time.

Example 7

Oxygen-delignified (O/O) mill sulphate pulp was bleached using different ozone and peracetic acid charges in Q-(OP)-Z/Paa/E_p sequences. The bleaching conditions are shown in Table 12.

Table 12. Chemical charges and reaction conditions used in the bleaching experiments.

Conditions (O/O pulp)	Q stage	(OP) stage	Z stage	Paa stage	E _p stage
Consistency %	8	12.5	12.5	10	10
NaOH, kg/BDt		20		2-7	8-17
Ozone, kg/BDt			0-10		
Peracetic acid, kg/BDt				0-20	
Peroxide, kg/BDt		20			3
MgSO ₄ , kg/BDt		2.5		2.5	2.5
DTPa, kg/BDt	3	2		2	
O ₂ pressure, bar		6			2
For pH adjustment	H ₂ SO ₄	NaOH	H ₂ SO ₄	NaOH/H ₂ SO ₄	NaOH
Initial pH	4.5		3.0	5.0	10.5
Temperature, °C	80	90	50	70	70
Reaction time, min	60	120	3-13	120-180	60

The results are presented in Table 13, while Figure 8 shows brightness development and Figure 9 the tear strengths of the resulting pulps.

Table 13. Characteristics of bleached sulphate pulps. 5/0 = reference, i.e. O/O-Q-(OP)-Z/E_p without peracetic acid.

O ₃ /Paa charge kg/BDt	Kappa no.	Bright. %	Visc. ml/g	Tear index (T70) mNm ² /g	Zero-span wet (T70), Nm/g
0/0	4.6	75.0	730	n.d.	n.d.
0/10	2.7	81.7	730	n.d.	n.d.
2.5/5	2.2	83.2	650	n.d.	n.d.
2.5/15	1.2	86.7	660	n.d.	n.d.
5/0	1.0	81.6	570	12.2	104
5/10	0.8	88.3	610	13.6	114
5/15	0.7	88.0	650	13.7	108
5/20	0.7	89.7	610	12.4	n.d.
7.5/5	0.6	89.3	590	12.0	n.d.
7.5/15	0.2	90.3	580	12.3	110
10/10	0.5	90.6	530	11.6	101

The results show that, in this case, the best strength characteristics and high brightnesses were obtained using the sequence O/O-Q-(OP)-Z/Paa/E_p according to the invention with an ozone charge of 5 kg/BDt and a peracetic acid charge of 10 - 15 kg/BDt.

Figure 8 presents the tear index of Z/Paa/EP pulp at a tensile index of 70 Nm/g for the different ozone and peracetic acid charges. It can be seen that the sequence O/OQ(PO)Z/Paa/EP led to tear index values about 2 units higher than with the O/OQ(PO)ZP sequence. The tear indexes compare with those of ECF pulps.

Figure 9 shows the zero-span tensile indexes (wet sheet) of Z/Paa/E_p pulp for different ozone and peracetic acid charges. The index reflects the strengths of individual fibres. The bleaching process according to the invention also improves the strengths of individual fibres.

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Patent claims:

1. A method for the production of bleached pulp with good strength characteristics in which
 - pulp is treated with ozone in at least one bleaching stage,

5 characterized in that

 - the ozone-treated pulp is brought into contact with a peroxy alkanoic acid under acidic conditions to reduce the alkali lability of the pulp, and
 - the pulp thus obtained is subjected to an alkali treatment stage.
- 10 2. A method according to claim 1, **characterized** in that ozone-treated pulp is treated with an oxidizing bleaching agent under alkaline conditions to reduce the amount of carbohydrates dissolving.
- 15 3. A method according to claim 2, **characterized** in that the amount of carbohydrates dissolved is reduced by at least 30 % compared with a situation in which the pulp is treated after the ozone stage under alkaline conditions.
- 20 4. A method according to claims 1, 2 or 3, **characterized** in that the pulp is kept at acid or neutral pH between ozone treatment and treatment with oxidizing bleaching agents.
5. A method according to claim 4, **characterized** in that the initial pH of the treatment with oxidizing bleaching agent carried out after ozone treatment is 4.5 - 8 and the final pH 2.5 - 6.
- 25 6. A method according to any one of claims 1-5, **characterized** in that ozone treatment and treatment with an oxidizing bleaching agent are conducted in the same bleaching stage.
- 30 7. A method according to any one of claims 1-6, **characterized** in that ozone treatment and treatment with an oxidizing bleaching agent are conducted at least essentially simultaneously.

8. A method according to any one of claims 1-6, **characterized** in that the pulp is treated first with ozone and then with an oxidizing bleaching chemical.

9. A method according to any one of claims 1-5, **characterized** in that ozone treatment and treatment with an oxidizing bleaching agent are carried out in different bleaching stages.

10. A method according to claim 9, **characterized** in that the pulp is washed between bleaching stages.

11. A method according to claim 10, **characterized** in that the pulp is washed with water between bleaching stages until it is more or less neutral.

12. A method according to any one of the foregoing claims, **characterized** in that the peroxy alkanoic acid used is a lower peroxy alkanoic acid, in particular peracetic acid.

13. A method according to claim 12, **characterized** in that the charge of peroxy alkanoic acid used is 1 - 40 kg per tonne (BDt) of pulp.

14. A method according to claim 12 or 13, **characterized** in that the ozone charge used corresponds to 30 - 90 % of the oxidation equivalents used in bleaching and that the charge of peroxy acid used corresponds to 70 - 10 % of the oxidation equivalents used in bleaching.

15. A method according to claim 14, **characterized** in that the ozone charge used corresponds to 40 - 70 % of the oxidation equivalents used in bleaching and that the charge of peroxy acid used corresponds to 60 - 30 % of the oxidation equivalents used in bleaching.

16. A method according to any one of the foregoing claims, **characterized** in that the alkaline treatment stage comprises an alkaline extraction stage, an oxygen stage, a hydrogen peroxide stage or a combination thereof.

17. A method according to claim 16, **characterized** in that the filtrate from the alkali extraction stage is recovered and at least a part of it recycled to the pulping stage or the bleaching stage.

5 18. A method according to claim 17, **characterized** in that the alkaline extraction stage is carried out after peroxy acid treatment without intermediate washing, in which case the filtrate from the alkaline extraction stage contains at least some peroxy acids, which lead to the formation of hydrogen peroxide.

10 19. A method according to claims 17 or 18, **characterized** in that the filtrate is recycled to the oxygen delignification stage.

20. A method according to any one of the foregoing claims, **characterized** in that the pulp to be bleached is treated with hydrogen peroxide prior to treatment with ozone.

15 21. A method according to claim 20, **characterized** in that the pulp to be bleached is treated with hemicellulase prior to treatment with hydrogen peroxide.

20 22. A method according to any one of the foregoing claims, **characterized** in that at least 10 %, preferably at least about 15 %, of the pulp's carbonyl groups are oxidized.

23. A method according to claim 22, **characterized** in that the pulp entering the alkali stage has a carbonyl group content of less than 14 mequ per kg when the pulp has been bleached with 625 kg of oxidation equivalents per tonne.

25 24. A method according to any one of the foregoing claims, **characterized** in that the pulp to be bleached is chemical pulp, chemi-mechanical pulp or mechanical pulp.

30 25. A method according to claim 24, **characterized** in that the pulp to be bleached is oxygen-delignified sulphate pulp.

26. A method according to any one of the foregoing claims, **characterized** in that the pulp to be bleached entering the ozone stage has a kappa number of 2 - 16, more particularly about 2 - 10.

5 27. A method according to any one of the foregoing claims, **characterized** in that the pulp is bleached to an ISO brightness of at least 85 %.

28. A pulp bleaching sequence, **characterized** in that the sequence is

10 -Z/Paa/P,
 -Z-Paa/P,
 -Z/Paa-P
 -Z/Paa/E,
 -Z/Paa-E,
15 -Z/Paa/EP,
 -Z/Paa/E_R

where Z indicates an ozone stage,

 Paa indicates a peroxy acid stage,

20 P indicates a peroxide stage (unpressurized or pressurized with
 oxygen),

 E indicates an alkaline extraction stage,

 R indicates an alkali stage involving the use of borohydride,

 O indicates an oxygen delignification stage, and

25 - indicates a washing stage.

29. A bleaching sequence according to claim 28, **characterized** in that it is preceded by a peroxide (P) or pressurized peroxide (PO) stage.

30 30. A bleaching sequence according to claim 29, **characterized** in that approximately 1 -

12 kg of ozone/BDt (0.1-1.2 %) is used in the ozone stage, approximately 1 - 3 kg of peroxy acid/BDt (0.1-3 %) is used in the peroxy acid stage, approximately 5 - 30 kg of hydrogen peroxide/BDt (0.5-3 %) is used in the peroxide stage preceding the ozone stage, and approximately 1 - 20 kg of hydrogen peroxide/BDt (0.1-2 %) is used in the peroxide stage following the peroxy acid stage.

31. A bleaching sequence according to claim 28, characterized in that it is preceded by one of the following sequences:

-O/O-X/Q-(PO),

-O/O-X/Q-P,

-O-O-Q-P or

-O/O-X-Z/Paa/Q-P,

where X indicates treatment of the pulp with an enzyme and

Q indicates an addition stage involving a complexing agent.

32. Ozone-bleached pulp, characterized in that its

- kappa number is less than 2,

- viscosity is greater than 600 ml/g,

- tear index (T70) is over 13 mN·m²/g and

- zero-span tensile index (T70) measured from a wet sheet is over 100 N·m/g.

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Kappa number

PO-pulp

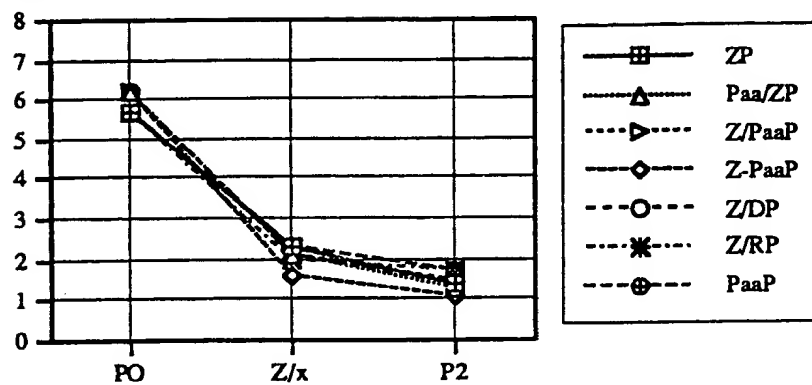


FIG. 1

Brightness, %

PO-pulp

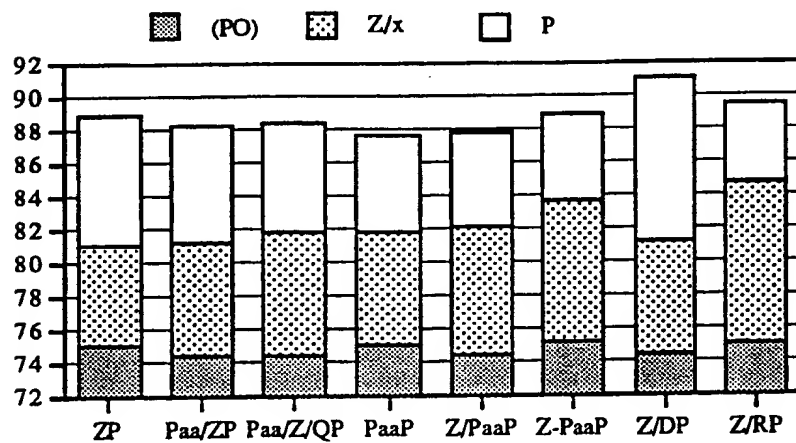
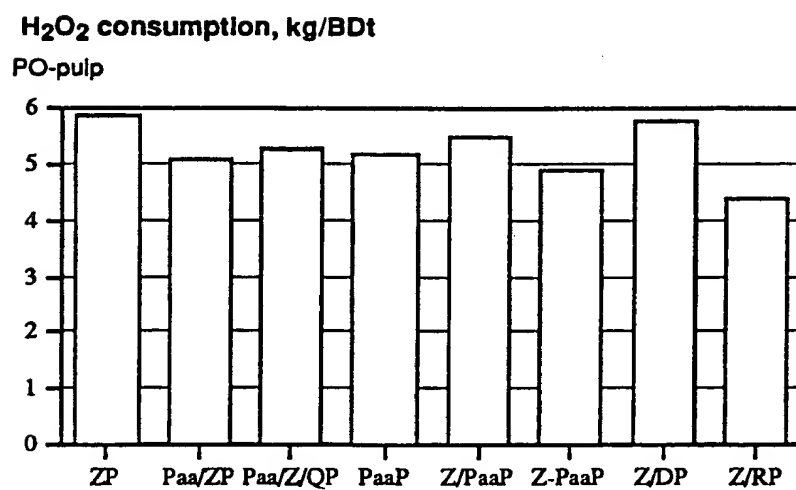
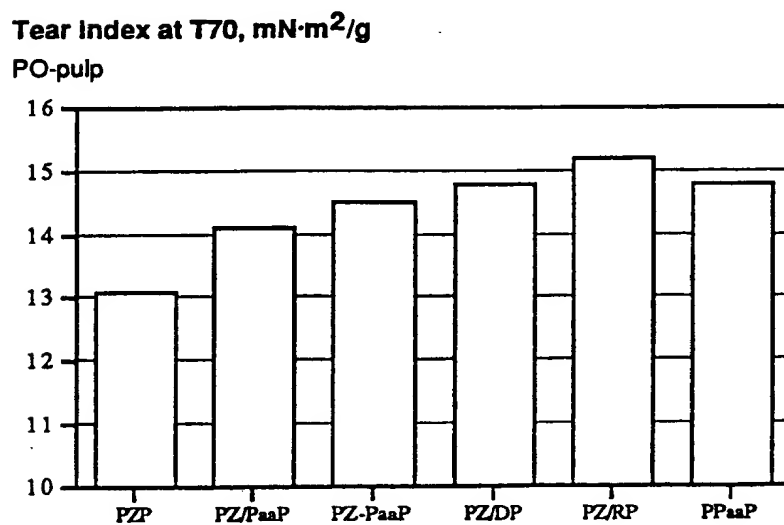
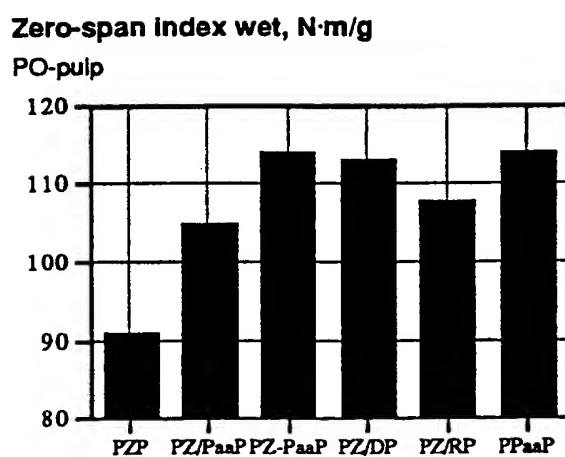


FIG. 2

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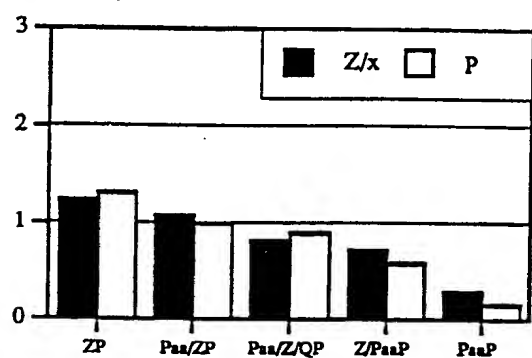
*FIG. 3**FIG. 4*

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*FIG. 5*

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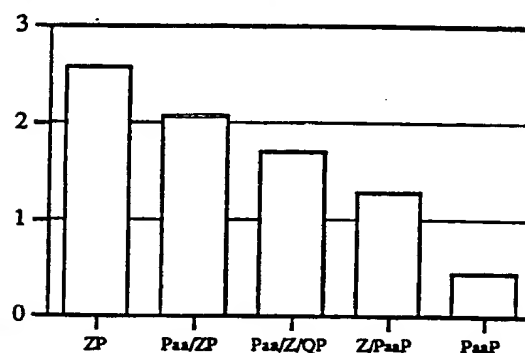
Carbohydrates dissolved in effluent, kg/tp
Mill P1 pulp



(a)

FIG. 6

Total carbohydrates dissolved in effluent, kg/tp
Mill P1 pulp, Z/x+ P stages



(b)

FIG. 7

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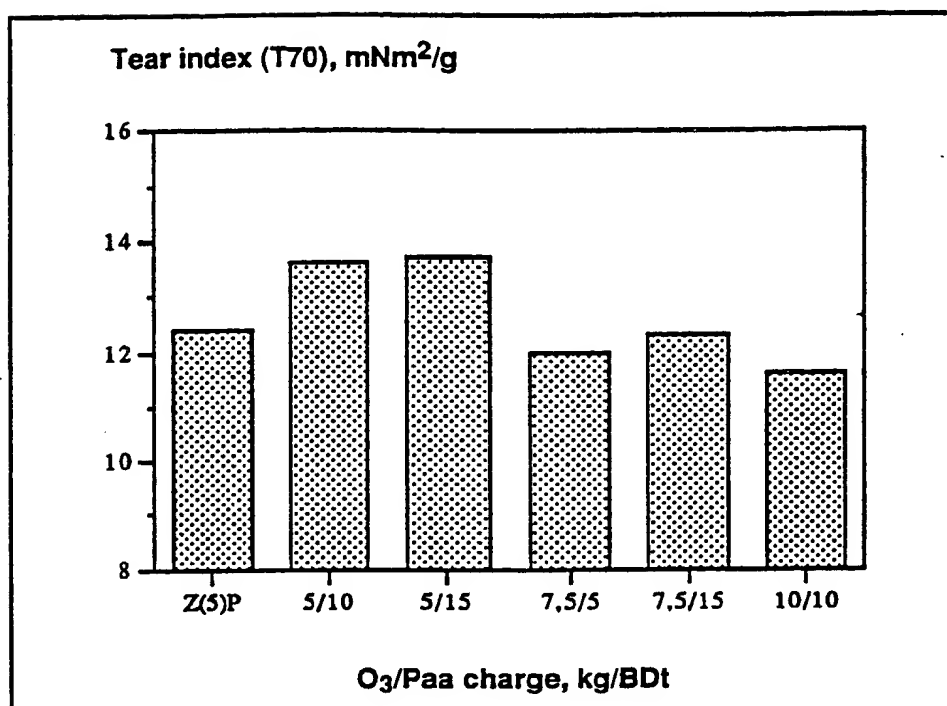


FIG. 8

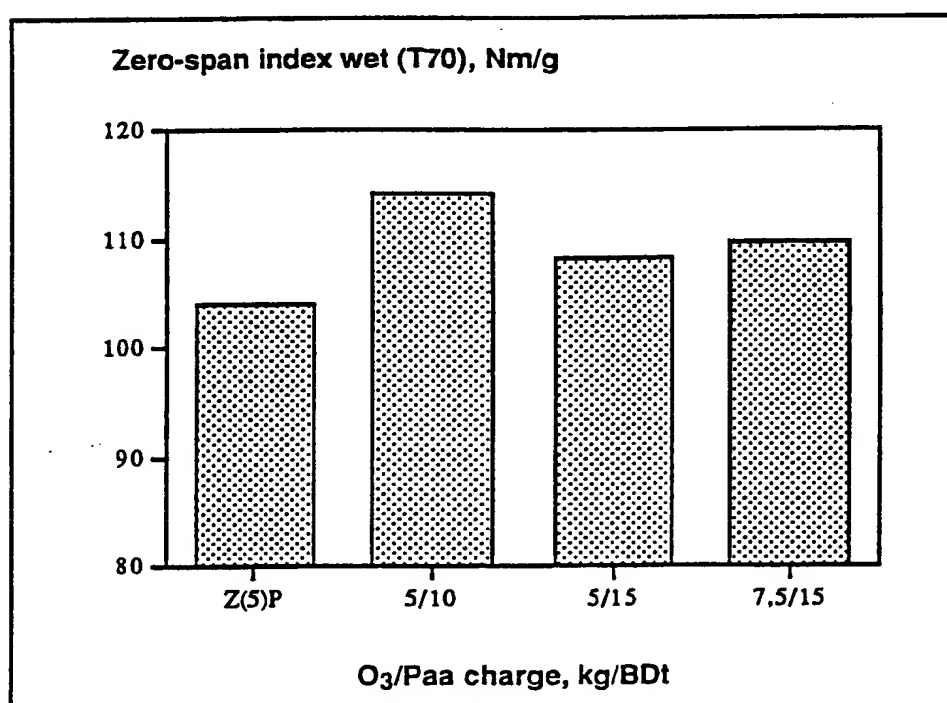


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00730

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/153, D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 9701667 A1 (SUNDS DEFIBRATOR INDUSTRIES AB), 16 January 1997 (16.01.97), whole document --	1-32
P,X	SE 9604511-7 A (AHLSTROM MACHINERY OY), 8 June 1997 (08.06.97), page 2, line 20 - line 37; page 3, line 1 - line 9; page 7, line 20 - line 23, page 14, line 24 - line 25; page 17, line 2 - line 3; page 19, line 1 - line 3; all claims --	1-32
X	US 5411635 A (RAYMOND C. FRANCIS ET AL), 2 May 1995 (02.05.95), page 4, line 40 - line 62; page 5, line 20 - line 23; page 5, line 50 - line 68, page 6, line 1 - line 2; page 7 line 57 - line 68, figur 6; all claims; abstract --	1-32

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

5 February 1998

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00730

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5387317 A (VENKETA R. PARTHASARATHY ET AL), 7 February 1995 (07.02.95), claim 11 --	1
A	WO 9221814 A1 (INTEROX INTERNATIONAL (SOCIETE ANONYME)), 10 December 1992 (10.12.92), whole document --	1-32
A	FR 2692917 A1 (L' AIR LIQUIDE), 31 December 1993 (31.12.93), page 2, line 1 - line 6 -- -----	1-32

INTERNATIONAL SEARCH REPORT
Information on patent family members

03/02/98

International application No.

PCT/FI 97/00730

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WO 9221814 A1	10/12/92	AT 127179 T AU 651462 B AU 1877592 A BE 1004974 A BR 9206112 A CA 2110698 A DE 69204457 D,T EP 0587822 A,B SE 0587822 T3 ES 2079209 T FI 935422 D JP 6507683 T NO 934406 A NZ 242996 A	15/09/95 21/07/94 08/01/93 09/03/93 10/10/95 10/12/92 18/04/96 23/03/94 01/01/96 00/00/00 01/09/94 26/01/94 27/01/95
FR 2692917 A1	31/12/93	NONE	